Analysis of organic compounds

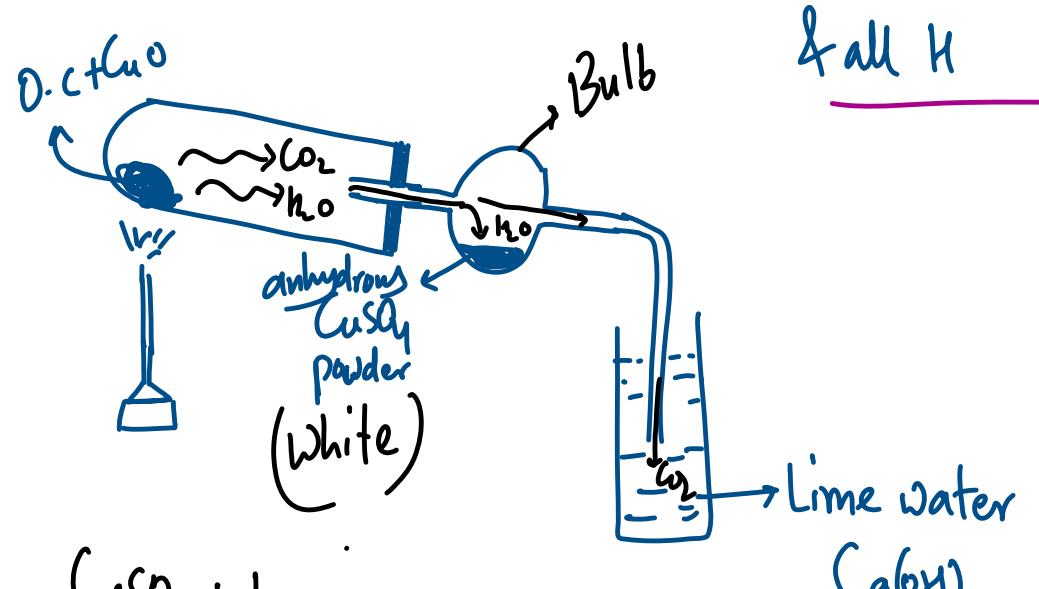
Thursday, January 19, 2023 6:15 PM

Organic Compound Analysis → Quantitative Analysis
↳ measurement of % of element in O.C

Qualitative Analysis
⇓
only detection of element in O.C (organic cpd)

O.C can have
↳ C, H, N, S, X(Halogen), P

1) C & H



$CuSO_4$ (White) $+ H_2O \rightarrow CuSO_4 \cdot 5H_2O$ (Blue)

$O.C + \overset{\boxed{O.A}}{CuO} \rightarrow \boxed{CO_2} + \boxed{H_2O} + Cu_2O/Cu$

(**) all Carbon converts to CO_2
& all H " " H_2O

$CO_2 + LiOH \rightarrow Li_2CO_3$

$CO_2 + \boxed{\overset{\ominus}{OH}} \rightarrow CO_3^{2-} + H_2O$

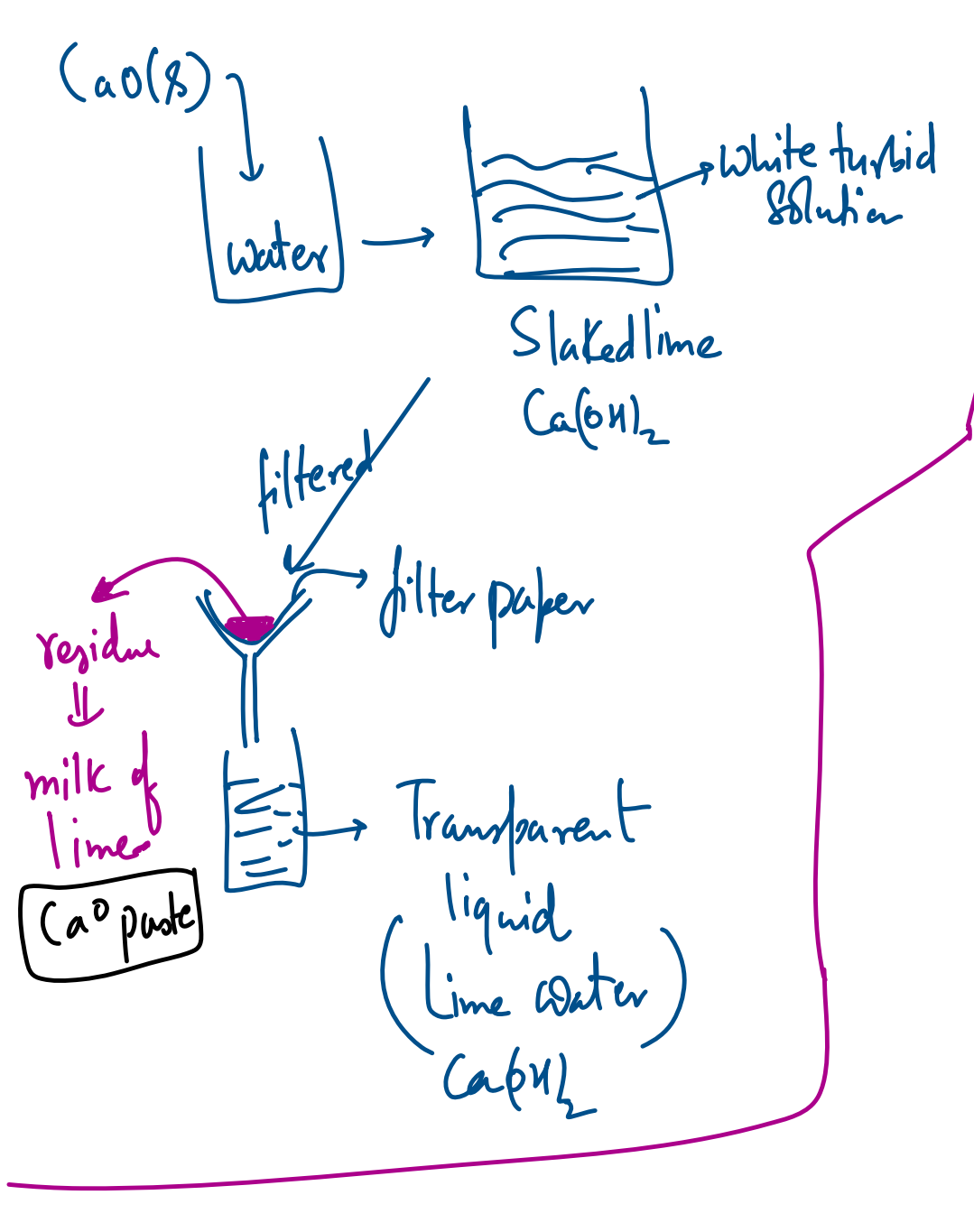
(**) $KO_2 + CO_2 \rightarrow K_2CO_3 + O_2$

CO_2 + Limewater → Milky Sol^n

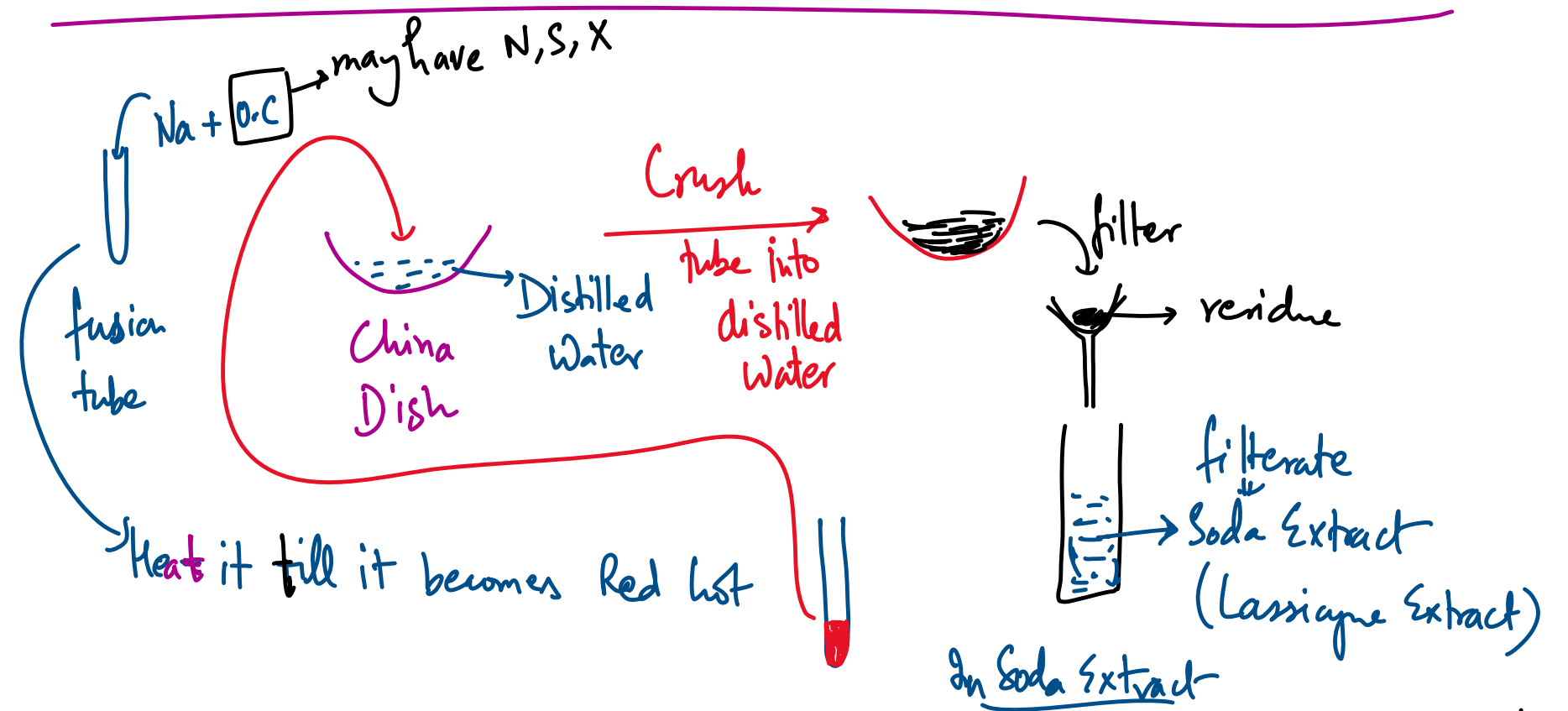
$\underset{H_2CO_3}{CO_2} + Ca(OH)_2 \rightarrow \underset{White}{CaCO_3} + H_2O$

Note:

$\underset{Limestone}{CaCO_3} \xrightarrow{\Delta} \underset{lime\ (Quick\ lime)}{CaO(s)} + CO_2\uparrow$



for $\boxed{N, S, X}$ detection, we prepare Lassaigne Extract or Soda Extract


Na + O.C → may have N, S, X
fusion tube
Heat it till it becomes Red hot
China Dish
Distilled water
Crush tube into distilled water
filter
residue
filtrate
Soda Extract (Lassaigne Extract)

In Soda Extract
$Na + C + N \rightarrow NaCN(aq)\ Na^+\ \overset{-}{CN}$
$Na + S \rightarrow Na_2S(aq)\ Na^+\ S^{2-}$
$Na + X \rightarrow NaX(aq)\ Na^+\ X^-$
$Na + S + N + C \rightarrow NaSCN(aq)\ Na^+\ \overset{\ominus}{SCN}$

Detection of N is possible by Soda Extract when C is present with N
CH_3NH_2 ✓
$NH_2\text{-}NH_2$ ✗ (N_2H_4)

① Detection of N in O.C

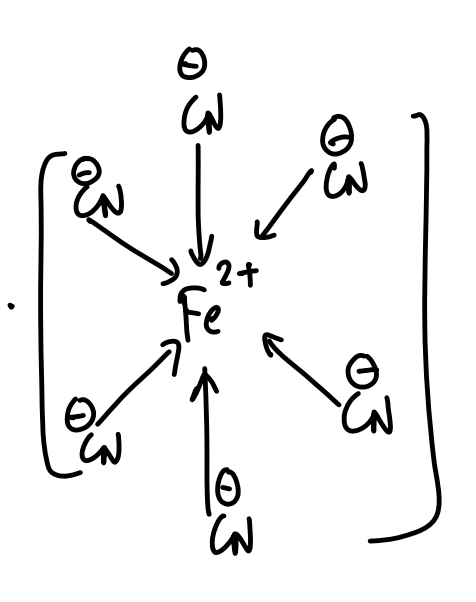
Take small amount of Soda extract (2ml)

$\boxed{\overset{+\ -}{NaCN}\ (Sod.\ Ext.)} + \boxed{FeSO_4 + NaOH}$ (freshly Prepared) $\xrightarrow{Boil}$ $Na^+ [Fe(CN)_6]^{4-}$
$Fe(OH)_2$ reacts with NaCN
⇓
$\boxed{Na_4[Fe(CN)_6](aq)}$ Sod. Ferrocyanide $Na^+\ [Fe(CN)_6]^{4-}$

$FeCl_3$, Fe^{3+} Salt ↙
Fe^{3+} ion replaces Na^+

$Fe^{3+}\ [Fe(CN)_6]^{4-}$

$\boxed{Fe_4[Fe(CN)_6]_3}$ ⇒ $4Fe^{3+}$ ·



Ferri Ferrocyanide
Prussian Blue Color
(Royal Blue Color)
↳ Its format^n Confirms N present with Carbon in O.C

② for S

take Small amount of Sod. Extract & treat with

ⓘ $Pb(CH_3COO)_2$ (Lead acetate)

$\underset{(Sod.\ Ext)}{Na_2S} + Pb(CH_3COO)_2 \rightarrow \overset{Black\ ppt}{\boxed{PbS}}\downarrow + CH_3COONa$

(ii) Sod. Nitroprusside $\boxed{Na_2[Fe(CN)_5NO]}$ ⇒ few drops are added to Soda Extract
$(+2) + x\ \ -5 + 1 = 0$

Coordination sphere

$Na_2\text{Ⓢ} + Na_2\boxed{[Fe(CN)_5\boxed{NO}]} \rightarrow 4Na^+[Fe(CN)_5\boxed{NOS}]^{-4}$
$\boxed{+2\ -5\ +1}$ $\overset{+}{NO}$ $+2\ -5\ +1\ -2$

$\boxed{Na_4[Fe(CN)_5NOS]}$
Violet Color

(#) If S is present along with N, then Soda Ext → $\boxed{NaSCN}$

$NaSCN + \underset{(FeCl_3)}{Fe^{3+}} \rightarrow \boxed{Fe(SCN)_3 \text{ or } [Fe(SCN)_6]^{3-}}$
Blood Red compound

③ for Halogen

we added $AgNO_3$ Sol^n to Sod. extract (NaX)

$NaX \xrightarrow{AgNO_3} \boxed{AgX}\downarrow + NaNO_3$

AgF → Water Soluble
AgCl → White ppt $\xrightarrow[NH_3(aq)]{or\ NH_4OH}$ AgCl dissolves ⇒ $[Ag(NH_3)_2]^+\ \overset{-}{OH}$
AgBr → Pale yellow ppt " → AgBr partially Soluble in $NH_3(aq)$
AgI → Dark yellow ppt " → AgI is insoluble in $NH_3(aq)$

Note: If S, N is also present along with Halogen, then Before Adding $AgNO_3$, we must decompose (NaCN), (Na_2S) by adding small amount of HNO_3 (Nitric Acid) & heated

$NaCN + HNO_3 \rightarrow HCN\uparrow + NaNO_3$
Na_2S + " $\rightarrow H_2S\uparrow + NaNO_3$

Otherwise, we would obtain

$NaCN + AgNO_3 \rightarrow \underset{white\ ppt}{AgCN}\downarrow + NaNO_3(aq)$
Na_2S + " $\rightarrow \underset{Black\ ppt}{Ag_2S}\downarrow + NaNO_3(aq)$

④ Test for Phosphorous

$\boxed{O.C\ having\ P} + \underset{Oxidising\ agent}{Na_2O_2} \rightarrow \overset{P^{+5}}{Na_3PO_4} + Na_2O$

$\overset{PO_4^{3-}}{Na_3PO_4} + Conc.\ HNO_3 + \underset{Amm.\ Molybdate}{\overset{\overset{\oplus}{NH_4}\ MoO_4^{2-}}{(NH_4)_2MoO_4}}$
↓
$(NH_4)_3PO_4 \cdot ⑫MoO_3$
Ammonium phosphomolybdate
(Yellow color)
Cannary

$\overset{S^{+6}}{SO_4^{2-}}$ → Sulphate
$\overset{P^{+5}}{PO_4^{3-}}$ → Phosphate
$\overset{Cr^{+6}}{CrO_4^{2-}}$ → Chromate
MoO_4^{2-} → Molybdate
WO_4^{2-} → Tungstate

Grp6
Cr → Chromium
Mo → Molybdnum
W → Tungstun

Quantitative Analysis → measurement of amount of element

Liebig's method
$\overset{O.C}{C} + CuO \rightarrow CO_2$
$H + CuO \rightarrow H_2O$

$\%C\ in\ O.C = \frac{wt.\ of\ C\ in\ O.C}{wt.\ of\ O.C} \times 100 = \frac{12 \times 1 \times wt.\ of\ CO_2}{44 \times wt.\ of\ O.C} \times 100$

$\%H\ in\ O.C = \frac{1 \times 2 \times wt.\ of\ H_2O}{18 \times wt.\ of\ O.C} \times 100$

Carius method
$S \rightarrow BaSO_4\ (M = 233\ g/mole) \Longrightarrow \%S\ in\ O.C = \frac{32 \times 1 \times wt.\ of\ BaSO_4}{233 \times wt.\ of\ O.C} \times 100$

$\underset{(in\ O.C)}{X} \xrightarrow{AgNO_3} AgX$ → AgCl (M = 143.5 g/mole) ⇒ $\%Cl\ in\ O.C = \frac{35.5 \times 1 \times wt(AgCl)}{143.5 \times wt.\ of\ O.C} \times 100$
→ AgBr (M = 188 g/mole)
→ AgI (M = 235 g/mole)

$\underset{(in\ O.C)}{P} \xrightarrow[\substack{MgCl_2 \\ heated}]{\substack{HNO_3 \\ + \\ NH_4Cl \\ +}} Mg_2P_2O_7$ $\boxed{M = 222\ g/mole}$ → $\%P = \frac{31 \times 2 \times wt(Mg_2P_2O_7)}{222 \times wt.\ of\ O.C} \times 100$
↳ Mag. Pyrophosphate

Note: Principle of atom Conversion (POAC)
Atom is neither created nor be destroyed, it jumps from one compound to other compound during Rx^n.

$\underset{(in\ O.C)}{C} \xrightarrow{CuO} CO_2$

(POAC for C) no. of C atoms in O.C = no. of C atoms in CO_2

$\boxed{no.\ of\ moles\ of\ C\ in\ O.C} = \boxed{no.\ of\ moles\ of\ C\ in\ CO_2}$

moles of C in CO_2 = no. of C × mole of CO_2

" = no. of C-atoms in CO_2 × $\boxed{moles\ of\ CO_2}$
" = 1 × moles of CO_2

$\frac{wt.\ of\ C\ in\ O.C}{12} = 1 \times \frac{wt.\ of\ CO_2}{44}$

$\boxed{wt.\ of\ C\ in\ O.C = \frac{12}{44} \times 1 \times wt.\ of\ CO_2}$

$\underset{(O.C)}{H} \rightarrow H_2O$

$\%H = \frac{1 \times 2 \times wt.\ of\ H_2O}{18 \times wt.\ of\ O.C} \times 100$

(#) for N determination

2 Methods

① DUMA's method
② Kjeldahl's Method

Ⓘ DUMA's Method

$\underset{(from\ O.C)}{N} + CuO \xrightarrow{\Delta} N_2$ gas is obtained at given T&P (V ml)

→ first Convert volume of N_2 from Given T&P to STP or NTP (P = 1 bar or 1 atm, T = 0°C → 273.15 K)

Note:- If aqueous Tension is given (V.P of H_2O)

$\boxed{P_{N_2} = P_{moist\ N_2} - Aq.\ Tension}$

moles of N_2 at Given T&P = moles of N_2 at STP

$\frac{P_1V_1}{T_1} = \left(\frac{P_2V_2}{T_2}\right)_{STP}$ $P_2 = 1\,atm$, $T_2 = 273.15\,K$

$V_2(Vol.\ at\ STP) = \frac{P_1V_1 \times T_2}{T_1 \times P_2}$

moles of N_2 at STP $= \frac{V(N_2\ at\ STP)}{22400\,ml}$ → ml

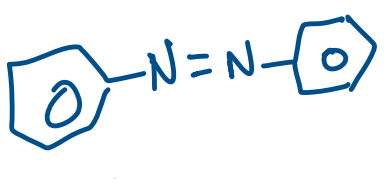
mole of N = 2 × moles of N_2
$= \frac{2 \times (V_{N_2}\ at\ STP)}{22400}$

wt. of N $= \frac{2 \times (V_{N_2}\ at\ STP)}{22400} \times 14$

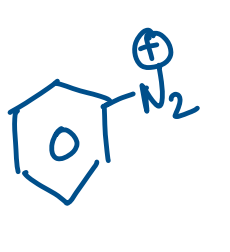
$\%N\ in\ O.C = \frac{wt.\ of\ N}{wt.\ of\ O.C} \times 100 = \frac{28 \times V_{N_2}(STP)}{22400} \times 100$ (in ml)

Ⓘⓘ Kjeldahl's Method
↳ used to estimate N in foods, fertilizers and drugs.
↳ not applicable for Compounds having (i) N in Ring eg Pyridine, pyrole, piperidine, Aziridine

(ii) Nitro(NO_2) compounds eg Nitrobenzene, Nitroalkane
(iii) Azo Compounds eg Azo Benzene
—N=N—



(iv) diazo "
$-\overset{+}{N}\equiv N$
eg



$\underset{in\ O.C}{N} \xrightarrow[to]{Converts} \underset{(aq)}{NH_3}$ or $\boxed{NH_4OH}$ ($n_f = 1$)
| Large amount of H_2SO_4(Conc.) → N_1, V_1(ml)
↓
$(NH_4)_2SO_4 + H_2O + (H_2SO_4$ remaining unreacted)
| Titrated with NaOH Sol^n → N_2, V_2(ml)
↓
meq(NaOH) = meq(H_2SO_4 remaining)
↳ N_2V_2

meq(NH_3) = meq(H_2SO_4 used)
= meq(H_2SO_4 Total) − meq(H_2SO_4 remaining)

$\underset{(NH_3)}{mmoles} \times n_f(NH_3) = (N_1V_1 - N_2V_2)$

$moles(NH_3) = \frac{N_1V_1 - N_2V_2}{1000}$

moles of N in NH_3 = moles of NH_3 $= \frac{N_1V_1 - N_2V_2}{1000}$

wt of N in NH_3 $= \frac{(N_1V_1 - N_2V_2)}{1000} \times 14$

$\%\ of\ N\ in\ O.C = \frac{wt.\ of\ N}{wt.\ of\ O.C} \times 100 = \frac{N_1V_1 - N_2V_2 \times \cancel{100} \times 14}{\cancel{1000} \times wt.\ of\ O.C}$

$\boxed{\%\ of\ N = \frac{(N_1V_1 - N_2V_2) \times 14}{10 \times wt.\ of\ O.C}}$
N_1V_1 → meq of H_2SO_4 Total
N_2V_2 → meq of NaOH

Example 16

$N_2V_2 = 0$
$N_1V_1 = 10 \times 1 \times 2 = 20$

$\%N = \frac{20 \times 14}{10 \times 0.5} = 56\%$

Example 17

wt. of O.C = 0.35 g
$N_1V_1 = 1\cancel{0}0 \times \frac{1}{\cancel{10}} \times 2$
$N_2V_2 = 154 \times \frac{1}{10} \times 1$

$\%N = \frac{(20 - 15.4) \times 14}{10 \times 0.35}$
$= \frac{4.6 \times 14 \times 100}{10 \times 35} = 18.4\%$

Solve Ex→9.6